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THE ROLE OF MINOR ATMOSPHERE ADMIXTURES IN THE  
ABSORPTION OF INFRARED RADIATION

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THE ROLE OF MINOR ATMOSPHERE ADMIXTURES IN THE  
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SUMMARY

The role of minor atmospheric gas admixtures in the absorption of infrared radiation is discussed from various points of view. The unavailability of practical methods of computations is emphasized. The transparency of minor atmospheric admixtures is plotted as a function of  $W/W_0$  and the errors of calculation are evaluated. It is concluded that minor atmospheric components play a significant role in the attenuation of infrared radiation.

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1. The minor atmospheric components  $N_2O$ ,  $CH_4$  and  $CO$ , as well as  $CO_2$  have an approximately constant relative concentration at various heights up to 50 km. For  $N_2O$  it constitutes  $\sim 0.27 \cdot 10^{-6}$  g/g, for  $CH_4$   $\sim 2.4 \cdot 10^{-6}$  g/g and for  $CO$   $\sim 1.1 \cdot 10^{-6}$  g/g [1]. In comparison with carbon dioxide, for which the concentration is  $\sim 320 \cdot 10^{-6}$  g/g, the  $N_2O$ ,  $CH_4$  and  $CO$  content in the atmosphere is negligible. Therefore for the solution of many problems of atmospheric optics the absorption of radiation by these components was generally not taken into account. However, minor admixtures must unquestionably play an essential role in absorption when radiation passes at various heights through the entire thickness of the Earth's atmosphere. An experimental solution of the stated problem in real conditions is beset with difficulty and high cost of the experiment; therefore, in the present investigation the problem is solved by means of computation.

2. At the present time there is in literature a series of investigations of spectral absorption of minor atmospheric components [2-4,6], nonetheless, practical methods for computations are absent.

Howard et al [7] have shown by means of experimental data processing that absorption of infrared radiation in rotation-vibra-

tion  $H_2O$  bands may be represented with an error not exceeding 5% in the form of a function of two parameter ratio: the mass  $W$  of absorbing gas on the radiation's path and the spectral parameter  $W_0$  equivalent to the mass of gas responsible for 50% of radiation absorption in the given wavelength at normal pressure. The obvious simplicity and convenience of such a presentation of functional dependence of water vapor absorption at sufficiently high precision of calculations would be desirable for the consideration of absorption by minor atmosphere components.

Laboratory data by Burch and Williams [3,4] obtained at normal pressure for all masses of absorbing gases and realized in the experiment, are presented in form of a function of ratio  $W/W_0$  in Fig.1. Experiments [3,4] were performed with values of  $N_2O$  mass from  $1 \cdot 10^{-3}$  to 10 atm·cm,  $CH_4$  from 0.134 to 188 atm·cm and CO from  $7 \cdot 10^{-2}$  to 11.40 atm·cm. In real conditions, possible mass values of these components lie respectively within the limits of 0-9 atm·cm, 0-80 atm·cm and 0.35 atm·cm, i.e. the aggregate of points in Fig.1 encompasses almost all possible amounts of absorbing substance in real atmosphere. The circles in the figure refer to various portions of spectrum in the 4.5 and 14.5 mkm absorption bands of  $N_2O$ , to the points of CO bands 2.34 and 4.66 mkm: the crosses correspond to 3.31, 6.5 and 7.65 mkm absorption bands of  $CH_4$ .

As in the case of  $H_2O$  of [7], the obtained combination of points represents an entirely specific functional dependence of transmission  $T$  of minor components on the ratio  $W/W_0$  with maximum point scattering not exceeding 8%. This dependence is described by a simple expression [8] (Fig.1, solid line):

$$T = (1 + W/W_0)^{-1} \quad (1)$$

in which the absorption coefficient is  $K_\lambda = 1/W_0$ .

The value of parameters  $W_0$  for certain absorption bands of minor atmosphere admixtures, found as a result of processing the experimental data of [3,4] are compiled in Table 1.

Both expression (1) or directly Fig.1, may be used for the estimate of transparency at passage of infrared radiation through inhomogeneous atmospheric paths by means of mass determination of the absorbing substance  $W$  at normal pressure, equivalent absorption-wise to the gas mass  $\omega$ , located over the inhomogeneous path. The determination of  $W$ , equivalent absorption-wise to  $\omega$ , is usually realized approximately by the effective mass method.

3. We shall estimate the error in computation introduced as a consequence of the approximation method by taking account of atmosphere inhomogeneity. If  $W$  is found as  $\omega(P/P_0)^n$ , then, as a rule, when converting the transmission at normal pressure  $P_0$  to the case

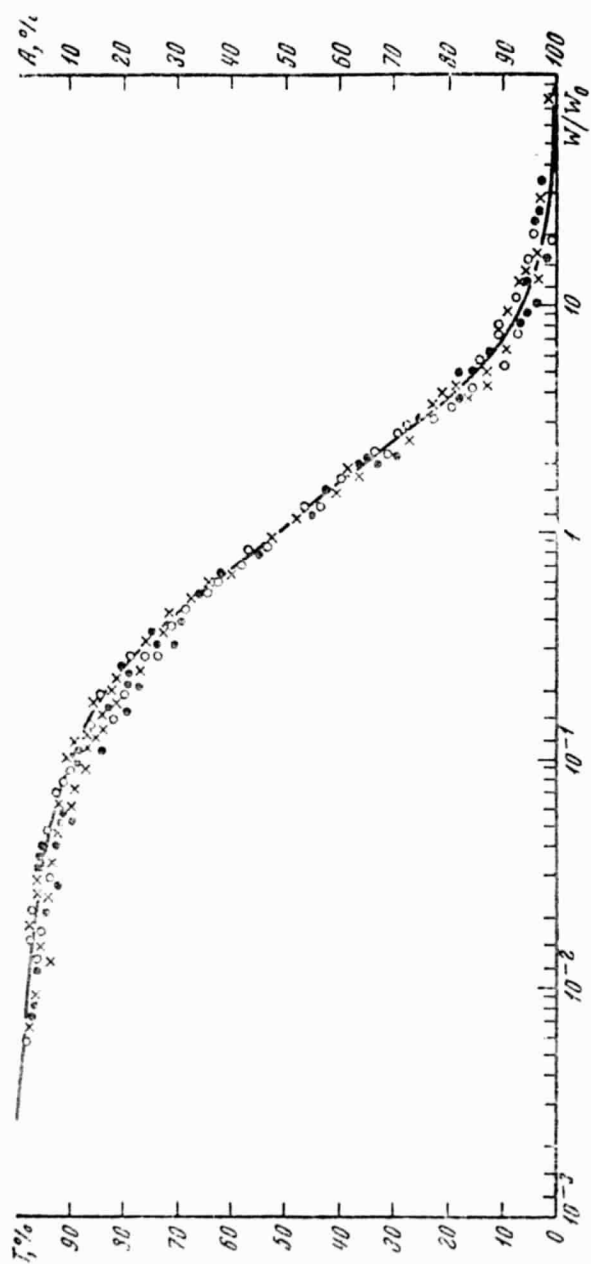


Fig. 1

Transmission function of minor atmosphere admixtures.

of pressure  $P$  for each concrete gas, a single invariable adjustment parameter  $\underline{n}$  is used in the assumption of its weak dependence on the wavelength, pressure and the absorbing mass.

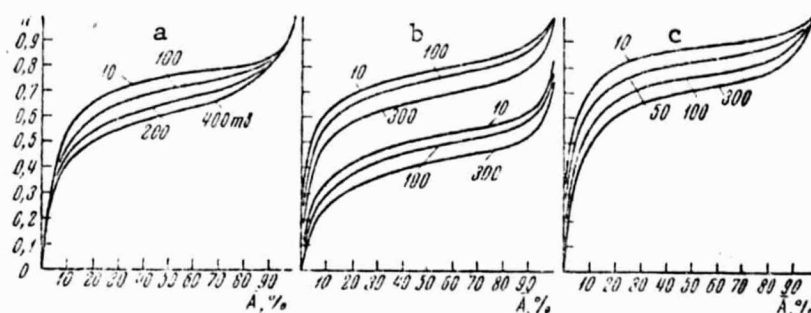


Fig. 2

Dependence  $n = f(\bar{A})$  for different absorption bands of minor components:

- a) 4.5 and 14.5 mkm  $N_2O$  bands,
- b) 3.31 and 7.65 mkm  $CH_4$  bands,
- c) 4.66 mkm  $CO$  band.

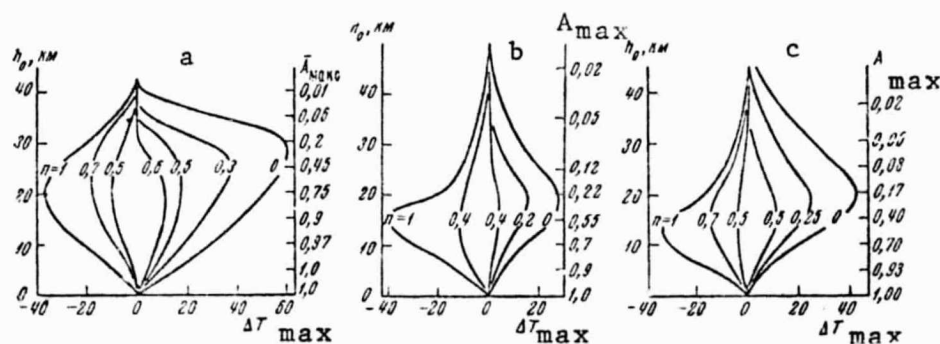


Fig. 3

Errors in computations of inhomogeneous path's transparency conditioned by the use of different indexes  $\underline{n}$ :

- a) 4.5 mkm  $N_2O$  band
- b) 3.31 mkm  $CH_4$  band
- c) 4.66 mkm  $CO$  band

The dependences of  $\underline{n}$  on  $\omega$  and  $P$  at the centers of  $N_2O$ ,  $CH_4$  and  $CO$  absorption bands may, however, be obtained as a result of processing the experimental data of [3,4], provided conditions  $A_1(W, P_0)$  are observed. Inasmuch as in the given frequency  $\omega$  and  $P$  determine the mean value of the absorption  $\bar{A}$ , whose accuracy of

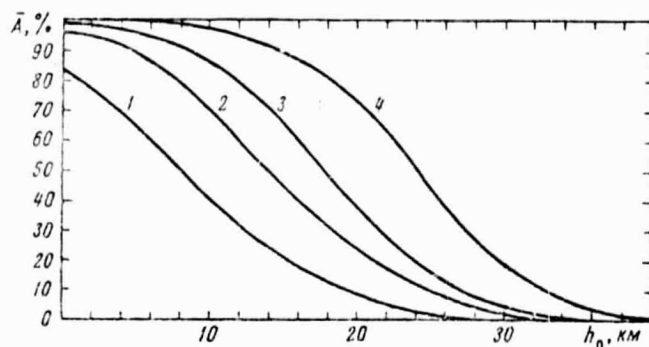


Fig. 4  
Dependence  $\bar{A} = \phi(h_0)$  for different absorption  
bands of minor admixtures

computation must be determined, it is practical to investigate the dependence of  $\underline{n}$  directly on  $\bar{A}$  for various  $P$ . The results of computations  $n = f(\bar{A})$  are presented in Fig. 2. In computations the values of  $\omega$  varied within the same limits as in the construction of Fig. 1, while the quantity  $P$  varied from 10 to 300-400 mb. The dependence of  $\underline{n}$  on higher pressures is not of interest, since the ratio  $P/P_0$  approaches the unity as the value of  $P$  approaches  $P_0$ . The obtained curves show that a relatively weak departure of  $\underline{n}$  from  $\omega$  (by no more than a factor of two) is observed at the centers of minor components' bands only in the region  $\bar{A}$  variation from 10 to 90%. The fluctuations of pressure from 10 to 400 mb lead respectively to the variation of  $\underline{n}$  by 1.3 - 1.5 times.

Thus strictly speaking, when taking into account the inhomogeneities of the atmosphere by the method of effective mass, the value of  $\underline{n}$  can not be assumed as invariable. However, considering the relatively weak variation of  $\underline{n}$  in the median region of values  $\bar{A}$ , and the increase in the influence on  $W$  as  $P$  increases, it is possible to select at the centers of  $N_2O$ ,  $CH_4$  and  $CO$  bands for a limited region of values  $\bar{A}$  a concrete invariable value of  $\underline{n}$ .

We shall now determine the greatest absolute errors  $\Delta T_{\max}$  in the computation of minor atmosphere component's transparency when using various constant values of  $\underline{n}$ . The greatest errors will take place at passage of the infrared radiation through the entire atmospheric thickness at the altitude  $h_0$  above the Earth's surface. as in such cases, the maximum possible values of  $\omega$  and  $\bar{A}_{\max}$  are realized. The results of computations of  $\Delta T_{\max}$  as a function of  $h_0$  are presented in Fig. 3 from which it may be seen that with the unfounded selection of the value of  $\underline{n}$ , the transmission of minor components may be either underrated to  $\Delta T_{\max} = 35-40\%$ , or overrated to  $\Delta T_{\max} = 30-60\%$ . When selecting the values of  $\underline{n}$ , taking into account the dependence  $n = f(\bar{A})$ , the additional error in the transparency over inhomogeneous paths introduced by the use of the appro-

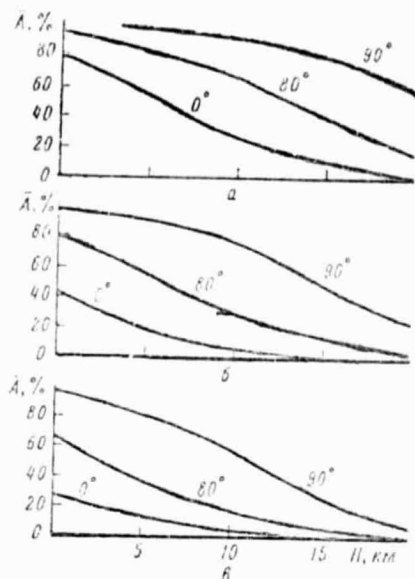


Fig.5

Variability of angular absorption of minor gas components at various levels in the atmosphere:

- a) 4.5 mkm  $N_2O$  band, b) 3.31 mkm  $CH_4$  band,  
c) 4.66 mkm  $CO$  band.

ximate method, will not exceed + 10%.

In this case it turns out that for the center of the 4.5 mkm  $N_2O$  band one may assume the value  $n = 0.6$ , for 14.5 mkm  $N_2O$  band, the value  $n = 0.5$  for the centers of the 3.31 mkm and 7.65 mkm  $CH_4$  bands, respectively the values  $n = 0.3-0.4$ ,  $n = 0.6-0.7$  and for the center of the 4.66 mkm  $CO$  band a value  $n = 0.5-0.6$ .

4. In conclusion we shall compute the transparency of  $N_2O$ ,  $CH_4$  and  $CO$  for various geometries of infrared radiation passage in the atmosphere.

The results of computations of absorption of radiation  $\bar{A}$  traversing the entire atmosphere thickness at altitudes  $h_0$  above the Earth's surface respectively for the centers of the bands: 14.5 mkm  $N_2O$  (curve 1), 3.31 mkm  $CH_4$  and 4.66 mkm  $CO$  (curve 2), 7.65 mkm  $CH_4$  (curve 3) and 4.5 mkm  $N_2O$  (curve 4) are presented in Fig.4.\*

Computations of  $\bar{A} = \phi(h_0)$  show that at transmission of infrared radiation near the Earth's surface ( $h_0 = 0$ ) both the weak (curves 1,2) and the strong absorption bands (curves 3,4) of minor atmosphere admixtures practically lead to total absorption of passing

\* Taking account of Earth's curvature and of infrared ray refraction [5].



radiation. A strong absorption, up to 40-98%, is retained as  $h_0$  increases up to 10 km. A sufficiently high transparency in the absorption region of minor components (above 80%) begins only with the values  $h_0 > 30$  km in the strong ones.

The results of computations of angular variability of minor gas components' absorption at various levels  $H$  in the atmosphere are presented in Fig.5. These computations are also evidence of substantial contribution of minor components to the weakening of infrared radiation, particularly for observation of zenithal angles  $Z$ , close to  $90^\circ$ .

T A B L E I

Value of parameter  $W_0$  for certain absorption bands of minor atmospheric admixtures

$\nu, \text{cm}^{-1}$	$\text{N}_2\text{O}$	$\nu, \text{cm}^{-1}$	$\text{CH}_4$	$\nu, \text{cm}^{-1}$	$\text{CH}_4$
500	$9.4 \cdot 10^4$	1040	$9.4 \cdot 10^4$	1500	$4.8 \cdot 10^2$
510	$6.2 \cdot 10^4$	1060	$1.6 \cdot 10^4$	1520	$1.4 \cdot 10^3$
520	$2.5 \cdot 10^4$	1080	$9.5 \cdot 10^3$	1540	$9.5 \cdot 10^1$
530	$3.7 \cdot 10^3$	1100	$4.7 \cdot 10^3$	1550	$3.1 \cdot 10^1$
540	$8.7 \cdot 10^1$	1120	$1.9 \cdot 10^3$	1560	$1.8 \cdot 10^2$
550	$2.7 \cdot 10^1$	1140	$9.5 \cdot 10^2$	1580	$1.4 \cdot 10^1$
560	$1.2 \cdot 10^1$	1160	$4.1 \cdot 10^2$	1600	$6.3 \cdot 10^2$
570	$5.8 \cdot 10^2$	1180	$2.4 \cdot 10^2$	1620	$4.7 \cdot 10^2$
580	$3.5 \cdot 10^2$	1200	$8.4 \cdot 10^1$	1640	$4.7 \cdot 10^2$
585	$5.4 \cdot 10^2$	1220	$2.2 \cdot 10^1$	1660	$8.0 \cdot 10^2$
590	$1.2 \cdot 10^2$	1230	$9.6 \cdot 10^2$	1670	$6.3 \cdot 10^2$
595	$3.7 \cdot 10^2$	1245	$1.0 \cdot 10^1$	1680	$8.0 \cdot 10^2$
600	$3.7 \cdot 10^2$	1270	$3.0 \cdot 10^2$	1700	$2.5 \cdot 10^3$
610	$6.6 \cdot 10^2$	1290	$4.1 \cdot 10^2$	1710	$2.4 \cdot 10^3$
620	$1.5 \cdot 10^1$	1270	$1.8 \cdot 10^2$	1720	$5.0 \cdot 10^3$
630	$7.0 \cdot 10^1$	1280	$2.7 \cdot 10^2$	1740	$6.2 \cdot 10^1$
640	$3.7 \cdot 10^2$	1300	$2.1 \cdot 10^2$	1760	$9.1 \cdot 10^4$
650	$4.7 \cdot 10^3$	1310	$3.7 \cdot 10^{-1}$		
660	$3.7 \cdot 10^3$	1320	$9.0 \cdot 10^2$		
670	$1.6 \cdot 10^3$	1340	$2.1 \cdot 10^2$		
680	$8.7 \cdot 10^2$	1350	$1.5 \cdot 10^2$		
690	$5.8 \cdot 10^2$	1360	$1.7 \cdot 10^2$		
692	$1.1 \cdot 10^2$	1380	$1.1 \cdot 10^1$		
695	$5.8 \cdot 10^2$	1400	$9.5 \cdot 10^1$		
710	$5.8 \cdot 10^2$	1420	$1.5 \cdot 10^2$		
720	$1.3 \cdot 10^3$	1440	$1.6 \cdot 10^2$		
730	$9.4 \cdot 10^3$	1460	$1.8 \cdot 10^2$		
740	$6.2 \cdot 10^4$	1480	$2.9 \cdot 10^2$		

Table continued.....

T A B L E I (continuation)

$\nu, \text{cm}^{-1}$	$\text{N}_2\text{O}$	$\text{CH}_4$	$\text{CO}$	$\nu, \text{cm}^{-1}$	$\text{N}_2\text{O}$	$\text{CH}_4$	$\text{CO}$
1950			$7.6 \cdot 10^3$	2210	$4.1 \cdot 10^{-2}$	$2.2 \cdot 10^4$	$9.2 \cdot 10^0$
1960			$6.1 \cdot 10^3$	2220	$4.1 \cdot 10^{-2}$	$2.1 \cdot 10^4$	$2.5 \cdot 10^1$
1970			$4.6 \cdot 10^3$	2224	$5.7 \cdot 10^{-2}$	—	—
1980			$3.0 \cdot 10^3$	2230	$4.9 \cdot 10^{-2}$	$2.0 \cdot 10^4$	$7.0 \cdot 10^1$
1990			$1.4 \cdot 10^3$	2240	$2.5 \cdot 10^{-2}$	$1.9 \cdot 10^4$	$2.0 \cdot 10^2$
2000			$7.6 \cdot 10^2$	2250	$4.3 \cdot 10^{-2}$	$1.7 \cdot 10^4$	$4.6 \cdot 10^2$
2010			$3.8 \cdot 10^2$	2260	$2.0 \cdot 10^{-1}$	$1.6 \cdot 10^4$	$2.3 \cdot 10^3$
2020			$2.0 \cdot 10^2$	2270	$2.3 \cdot 10^0$	$1.4 \cdot 10^4$	$7.6 \cdot 10^3$
2030			$1.1 \cdot 10^2$	2280	$2.5 \cdot 10^1$	$1.2 \cdot 10^4$	
2040			$6.5 \cdot 10^1$	2290	$3.8 \cdot 10^2$	$1.1 \cdot 10^4$	
2050			$3.4 \cdot 10^1$	2300	$1.9 \cdot 10^3$	$9.5 \cdot 10^3$	
2060			$1.6 \cdot 10^1$	2320		$7.9 \cdot 10^3$	
2070			$7.6 \cdot 10^0$	2340		$6.3 \cdot 10^3$	
2080			$4.6 \cdot 10^0$	2360		$5.0 \cdot 10^3$	
2090			$3.1 \cdot 10^0$	2380		$3.8 \cdot 10^3$	
2100	$1.4 \cdot 10^3$	$6.3 \cdot 10^4$	$1.8 \cdot 10^0$	2400		$2.7 \cdot 10^3$	
2110	$9.7 \cdot 10^2$	$5.5 \cdot 10^4$	$1.5 \cdot 10^0$	2420		$1.6 \cdot 10^3$	
2120	$5.8 \cdot 10^2$	$4.7 \cdot 10^4$	$1.5 \cdot 10^0$	2440		$1.3 \cdot 10^3$	
2130	$2.9 \cdot 10^2$	$4.2 \cdot 10^4$	$2.4 \cdot 10^0$	2460		$1.1 \cdot 10^3$	
2140	$8.3 \cdot 10^1$	$3.8 \cdot 10^4$	$4.1 \cdot 10^0$	2480		$9.0 \cdot 10^2$	
2150	$2.1 \cdot 10^1$	$3.4 \cdot 10^4$	$2.4 \cdot 10^0$	2500		$7.0 \cdot 10^2$	
2160	$6.5 \cdot 10^0$	$3.1 \cdot 10^4$	$1.1 \cdot 10^0$	2520		$6.0 \cdot 10^2$	
2170	$1.9 \cdot 10^0$	$2.9 \cdot 10^4$	$1.06 \cdot 10^0$	2540		$5.1 \cdot 10^2$	
2180	$3.7 \cdot 10^{-1}$	$2.7 \cdot 10^4$	$1.4 \cdot 10^0$	2560		$4.0 \cdot 10^2$	
2190	$1.5 \cdot 10^{-1}$	$2.5 \cdot 10^4$	$2.4 \cdot 10^0$	2580		$3.0 \cdot 10^2$	
2200	$6.2 \cdot 10^{-2}$	$2.3 \cdot 10^4$	$4.8 \cdot 10^0$	2600		$2.8 \cdot 10^2$	
				2620		$1.9 \cdot 10^2$	

$\nu, \text{cm}^{-1}$	$\text{CH}_4$	$\nu, \text{cm}^{-1}$	$\text{CH}_4$	$\nu, \text{cm}^{-1}$	$\text{CO}$
2640	$3.5 \cdot 10^2$	3240	$1.1 \cdot 10^3$	4120	$4.8 \cdot 10^4$
2660	$1.6 \cdot 10^2$	3260	$3.8 \cdot 10^3$	4130	$2.4 \cdot 10^4$
2680	$1.9 \cdot 10^2$	3280	$9.4 \cdot 10^3$	4140	$1.2 \cdot 10^4$
2700	$1.4 \cdot 10^2$	3300	$1.2 \cdot 10^4$	4150	$5.7 \cdot 10^3$
2720	$1.4 \cdot 10^2$	3320	$1.9 \cdot 10^4$	4160	$2.8 \cdot 10^3$
2740	$1.4 \cdot 10^2$	3340	$2.7 \cdot 10^4$	4170	$1.4 \cdot 10^3$
2760	$9.4 \cdot 10^1$	3360	$3.8 \cdot 10^4$	4180	$8.9 \cdot 10^2$
2780	$6.3 \cdot 10^1$	3380	$4.7 \cdot 10^4$	4190	$5.7 \cdot 10^2$
2800	$3.8 \cdot 10^1$	3400	$6.3 \cdot 10^4$	4200	$4.7 \cdot 10^2$
2820	$3.8 \cdot 10^1$			4210	$3.8 \cdot 10^2$
2840	$2.3 \cdot 10^1$			4220	$3.2 \cdot 10^2$
2860	$3.8 \cdot 10^0$			4230	$2.8 \cdot 10^2$
2880	$1.7 \cdot 10^1$			4240	$3.2 \cdot 10^3$
2900	$1.3 \cdot 10^1$			4250	$5.7 \cdot 10^2$
2920	$1.0 \cdot 10^1$			4255	$7.1 \cdot 10^2$
2940	$8.8 \cdot 10^0$			4260	$5.2 \cdot 10^2$
2960	$6.9 \cdot 10^0$			4270	$2.4 \cdot 10^2$
2980	$6.7 \cdot 10^0$			4280	$1.7 \cdot 10^2$
3000	$7.6 \cdot 10^0$			4290	$1.7 \cdot 10^2$
3020	$3.8 \cdot 10^0$			4300	$1.9 \cdot 10^2$
3040	$7.0 \cdot 10^0$			4310	$3.6 \cdot 10^2$
3060	$1.0 \cdot 10^1$			4320	$8.9 \cdot 10^2$
3080	$7.6 \cdot 10^0$			4330	$1.9 \cdot 10^3$
3100	$6.3 \cdot 10^0$			4340	$4.1 \cdot 10^3$
3120	$7.6 \cdot 10^0$			4350	$1.4 \cdot 10^4$
3140	$1.1 \cdot 10^1$			4360	$2.4 \cdot 10^4$
3160	$1.9 \cdot 10^1$			4370	$4.8 \cdot 10^4$
3180	$3.8 \cdot 10^1$				
3200	$9.5 \cdot 10^1$				
3220	$4.7 \cdot 10^1$				

### CONCLUSIONS

1. The interpretation of transparency of minor atmosphere admixtures in the form of function of  $W/W_0$  shows a sufficiently specific dependence with maximum scattering of points not exceeding 8%, which could be described by an analytical expression.

2. Taking into account the atmospheric inhomogeneties by the method of effective mass, the unfounded selection of indexes  $n$  may lead at the computation of transparency  $T$  to substantial errors.

3. If the average absorption of radiation  $\bar{A}$  at the center of the  $N_2O$ ,  $CH_4$  and  $CO$  bands varies from 10 to 90%, it is possible to select the value of  $n$  in such a manner, that the possible maximum absolute error in the computations of transmission will not exceed  $\pm 14\%$  of the aggregate error of functional representation of transparency in the form  $T = F(W/W_0)$  ( $\pm 4\%$ ) and the error resulting in the neglect of the variability of  $n$  from  $\omega$  and  $P$  ( $\pm 10\%$ ).

4. The accounting of the variability of  $n$  from  $\omega$  and  $P$  according to the dependence  $n = f(\bar{A})$  underrates the maximum error in transparency computations of minor components to  $\pm 5-7\%$ .

5. The computation of transparency of different air masses at the centers of the  $N_2O$ ,  $CH_4$  and  $CO$  absorption bands attests to the significant role of minor atmospheric components in the weakening of infrared radiation.

\* \* \* \* \* THE END \* \* \* \* \*

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